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**CHARACTERIZATION OF RECHARGEABLE
LITHIUM CELLS.
PART 1. LITHIUM/NIOBIUM TRISELENIDE CHEMISTRY**

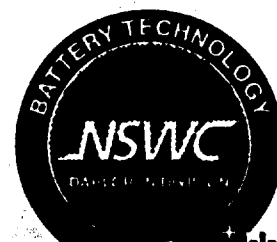
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WEAPONS RESEARCH AND TECHNOLOGY DEPARTMENT

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**NAVAL SURFACE WARFARE CENTER
DAHLGREN DIVISION • WHITE OAK DETACHMENT
Silver Spring, Maryland 20903-5640**



FOREWORD

Rechargeable lithium batteries offer many advantages over conventional battery systems currently being used in the Navy. They have higher voltages and greater energy densities but are a relatively new technology and must be thoroughly characterized prior to use in the fleet. This report summarizes cell testing results on lithium/niobium triselenide (Li/NbSe₃). The authors acknowledge the sponsorship of the Office of Naval Research under the High Energy Battery Project.

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ABSTRACT

The Naval Surface Warfare Center is evaluating industry's emerging lithium rechargeable battery technology for use in underwater vehicle applications. The battery industry typically characterizes cells for consumer applications requiring low rate cycling at room temperature and rarely provides high rate, low temperature data. High rate and low temperature performance of AT&T's lithium/niobium triselenide (Li/NbSe_3) AA cells is reported here. At 25°C and 10 mA/cm² (approximately the 3C rate), delivered energy densities were as high as 30 Wh/lb. However, these lithium cells proved vulnerable to performance loss in low temperature (0°C), high discharge rate cycling.

CONTENTS

<u>Section</u>	<u>Page</u>
INTRODUCTION	1
EXPERIMENTAL	2
CELL CONSTRUCTION	2
TEST EQUIPMENT	2
CYCLING PROCEDURES	2
RESULTS AND DISCUSSION	3
CONCLUSIONS	5
REFERENCES	17
DISTRIBUTION	(1)

ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	NbSe ₃ UNIT CELL	6
2	DISCHARGE CHARACTERISTICS OF Li/NbSe ₃ AA CELLS AT 1mA/cm ² , 75% DOD, AND 25°C. CELLS WERE CYCLED BETWEEN 2.40 AND 1.55V AND CHARGED AT 0.33mA/cm ²	7
3	DISCHARGE CHARACTERISTICS OF Li/NbSe ₃ AA CELLS AT 1mA/cm ² , 50% DOD, AND 25°C. CELLS WERE CYCLED BETWEEN 2.40 AND 1.74V AND CHARGED AT 0.33mA/cm ²	8
4	DISCHARGE CHARACTERISTICS OF Li/NbSe ₃ AA CELLS AT 5mA/cm ² , 75% DOD, AND 25°C. CELLS WERE CYCLED BETWEEN 2.40 AND 1.27V AND CHARGED AT 0.33mA/cm ²	9
5	DISCHARGE CHARACTERISTICS OF Li/NbSe ₃ AA CELLS AT 10mA/cm ² , 75% DOD, AND 25°C. CELLS WERE CYCLED BETWEEN 2.40 AND 1.00V AND CHARGED AT 0.33mA/cm ²	10
6	DISCHARGE CHARACTERISTICS OF Li/NbSe ₃ AA CELLS AT 5mA/cm ² , 50% DOD, AND 25°C. CELLS WERE CYCLED BETWEEN 2.40 AND 1.51V AND CHARGED AT 0.33mA/cm ²	11
7	DISCHARGE CHARACTERISTICS OF Li/NbSe ₃ AA CELLS AT 10mA/cm ² , 50% DOD, AND 25°C. CELLS WERE CYCLED BETWEEN 2.40 AND 1.37V AND CHARGED AT 0.33mA/cm ²	12
8	DISCHARGE CHARACTERISTICS OF Li/NbSe ₃ AA CELLS AT 1mA/cm ² , 75% DOD, AND 0°C. CELLS WERE CYCLED BETWEEN 2.40 AND 1.25V AND CHARGED AT 0.33mA/cm ²	13
9	DISCHARGE CHARACTERISTICS OF Li/NbSe ₃ AA CELLS AT 5mA/cm ² , 75% DOD, AND 0°C. DISCHARGE HALTED WHEN 0.80V MINIMUM WAS REACHED (BEFORE 75% DOD ACHIEVED) ...	14

TABLES

<u>Table</u>		<u>Page</u>
1	CYCLE LIFE OF Li/NbSe ₃ AA CELLS AND FAILURE MODE	15
2	SPECIFIC ENERGIES OF Li/NbSe ₃ AA CELLS	16

INTRODUCTION

This study is part of an on going effort to characterize state-of-the-art experimental lithium (Li) rechargeable AA cells. The objective is to test the cells in a manner which would allow for a fair comparison to other new battery systems for potential naval applications. The system to be discussed here is the experimental rechargeable lithium-niobium triselenide (Li/NbSe₃) cell manufactured by AT&T Bell Laboratories. These cells were distributed for evaluation only, and are not commercially available.

Niobium triselenide has been identified as a high energy density intercalation cathode material for ambient temperature Li rechargeable batteries. It consists of face sharing trigonal prismatic MX₆ units which form a fibrous ribbon-like morphology.^{1,2} The niobium triselenide unit cell is shown in Figure 1. Analysis of this structure reveals a lack of Nb-Nb bonds which free d-electrons to form metallic conduction bands.³ The conductivity of NbSe₃ is on the order of 2.9×10^2 ohm⁻¹ cm⁻¹ and still relatively high after Li insertion during discharge (Li₃NbSe₃ = 1×10^{-1} ohm⁻¹ cm⁻¹).^{4,5,6} As a result, no conducting additives are required to enhance conductivity. Graphite is commonly added to less conductive cathode materials to enhance conductivity. NbSe₃ does not exist freely in nature. It is typically prepared in the laboratory by placing stoichiometric amounts of niobium (Nb) foil and selenium (Se) granules or premixed Nb and Se powders in evacuated sealed quartz ampules. The ampules are then maintained at 670°C for 7-15 days.^{2,7,8,9} Hair-like fibers begin to grow and intertwine to form a structurally tough and electrically conductive mat. These needle-like fibers have been revealed by SEM analysis.⁷ This material can then be used without the aid of structural binders, and it maintains this fibrous morphology upon cycling. Due to its high surface area and good electrolyte penetration, high currents can be achieved.

Lithium intercalates into NbSe₃ at a 3:1 ratio giving Li₃NbSe₃.^{10,11} Its theoretical energy density approaches 200 Wh/lb.^{12,13,14} The electrochemical reduction of NbSe₃ in lithium ion + containing solutions is believed to occur in two steps.

Ratnakumar, et al.^{7,11,15} have determined by coulometric titration that approximately 0.6 equivalents of Li are intercalated in the first step of the reduction process between open circuit voltage (OCV) and 1.7V. Then approximately 1.8 equivalents intercalate between 1.7 and 1.55V. Below 1.55V another 0.25 equivalents can intercalate. This evidence would tend to confirm a multi-step reduction where one Li intercalates at one type of site and two Li's intercalate at a second site. After the first cycle, discharge curves exhibit only a single, slightly sloping voltage plateau, giving the false impression of a single, 3 Li equivalent intercalation process. NbSe₃ has a much higher voltage and energy density after the first cycle. This is attributed to a beneficial structural change upon lithiation which has been observed by others.^{4,6,7,9,11,12,16} X-ray diffraction analysis reveals amorphous diffraction patterns,^{7,9} indicating a loss of long-range crystallographic order.

EXPERIMENTAL

CELL CONSTRUCTION

The NbSe_3 cells characterized in this report were manufactured between November and December 1987, and were received by NSWCDD White Oak Detachment in December 1987. Testing began 4 to 8 months later, depending on the particular cell. They were cylindrical, spiral wrap, AA configuration, and 1.965-inches high by 0.565-inches in diameter. The average cell weight was 19.3 grams with an average OCV of 2.19V. There was a stainless steel disc vent rated at 250 to 300 psi at the cell bottom. The can and positive terminal were also stainless steel. Li and NbSe_3 weights were approximately 1.02 g and 5.1 g, respectively, which corresponds to a 220 percent excess of Li. The electrolyte is composed of equal volumes of propylene and ethylene carbonates, along with lithium/hexafluoroarsenate (LiAsF_6) and triglyme ether. Polypropylene (0.001-inch Celgard 2400) is used as the separator. The average working surface area of the cathode was 290 cm^2 . The manufacturer listed capacity at 1.2 Ah.

TEST EQUIPMENT

Cells under test were mounted on breadboards placed in an environmental chamber (Tenney Engineering Inc., Union, NJ). The leads from the breadboard were connected to an automated battery cycler (Techware Systems Corp., Vancouver, Canada). The battery cycle's computer software allows all cycling conditions to be programmed and executed automatically. Data sampling by the computer occurs at programmed time intervals and is stored on a hard disk instantaneously.

CYCLING PROCEDURES

As far as possible, different chemistries are tested under the same conditions to allow a fair comparison of their capabilities. All cells are AA size, hermetically sealed and of jellyroll construction. The test matrix employs three cells per condition and covers three discharge rates (1, 5, and 10 mA/cm^2), two depths of discharge (50 and 75 percent depth of discharge (DOD), and two cycling temperatures (0 and 25°C). It should be noted that the matrix is designed to test different Li battery chemistries in a similar manner and it may not follow the manufacturer's recommendations for ideal cycling conditions. However, the charge sequence recommended by the manufacturer is followed since past mishaps with rechargeable Li batteries have occurred during charging. In setting cycling currents, the manufacturer's figures for the working, cathode area of their AA cells are used. Under all cycling conditions, the charging current density and endpoint voltage (V_c) are the same, equal to the values recommended by the manufacturers. Cells are discharged to an endpoint voltage (V_d) corresponding to that obtained at the end of the first discharge (to the nominal DOD). Three cells are used to obtain an average value for V_d . Cycling is halted when discharge capacity to V_d fell to 25 percent of its first cycle value. Thus,

in nominally "75 percent DOD" cycling the actual DOD falls from the initial 75 percent to a final 25 percent of 75 percent = 18.75 percent (likewise, during "50 percent DOD" cycling, actual DOD goes from 50 to 12.5 percent). The charge procedure used for NbSe₃ followed the manufacturer's recommendation of 100 mA to a 2.4V cutoff. A second halt condition ends cycling during charging if the charge capacity rises to a value 20 percent larger than the charge capacity measured on the second cycle. A sudden increase in charge capacity may indicate the presence of dendrite shorting and cause cell venting. Charge and discharge succeeded each other without pause.

RESULTS AND DISCUSSION

Figure 2 shows the discharge curves of the cells at a discharge rate of 1mA/cm², 75 percent depth of discharge, and 25°C. Immediately evident is the significantly lower first cycle voltage. The voltage increased with each cycle until a maximum voltage was achieved near cycle 50. Capacity also increased slightly from 0.94 Ah to near 1.0 Ah before falling. This particular test achieved 200 cycles before it met the overcharge halt condition at a point where the discharge capacity had only faded to about 0.75 Ah. (See Experimental Section.) The highest mid-discharge voltage achieved was 1.95V. Thus, clearly there is some kind of a beneficial transformation occurring from cycle 1 to cycle 50. The depth of discharge may affect the rate at which the maximum voltage is achieved. The cell delivered 42 Wh/lb at cycle 100. Specific energy was calculated using equation (1).

$$(V_{1/2} \times I \times t) / W \quad (1)$$

Where $V_{1/2}$, I, t, and W are mid-cycle discharge voltage (volts), current (amps), time (hours), and weight (pounds), respectively. Table 1 shows the cycle life and failure mode of all cells used in this study at 25° and 0°C. The overcharge problem is believed to be caused by the shorting of Li dendrites through the separator material. A few cells (not shown in the table) did not cycle at all and were replaced. For reasons unknown, the battery cycler was unable to control the current in these cells and automatically stopped the test. On lowering the depth of discharge to 50 percent, leaving the temperature and current density unchanged, an unexpected decrease in cycle life was observed. The cell cycling shown in Figure 3 was halted by overcharge after only 50 cycles. The other two cells in this group lasted 32 and 22 cycles respectively ending by the same overcharge halt. Once again the capacity and discharge voltage increased with cycle number until the test was halted prematurely at cycle 50.

As current density increases from 1 mA/cm² through 5 mA/cm² and up to 10 mA/cm² (Figures 2, 4, 5 and 3, 6, 7) at 50 or 75 percent depth of discharge and 25°C, a pronounced dip in the first cycle voltage appears. This is speculated to be an anode film or the initial response to the load current by an unlithiated NbSe₃ cathode structure in a fresh uncycled cell. This effect is only present on cycle one and the voltage drop is larger at the higher discharge currents. At 75 percent DOD, the middle cycle voltages were 1.7V at 5 mA/cm² and 1.4V at 10 mA/cm². As expected, more cycles were obtained at 50 percent DOD than at 75 percent DOD for both the 5 mA/cm² and 10 mA/cm² cells. This is the opposite of the unusual behavior at 1 mA/cm² and 25°C where the cycle life significantly decreased at 50 percent DOD.

Although there were no pause times programmed into the cycling tests, cycling was periodically interrupted by power failures which open-circuited the cells. This is apparent in Figures 6, 7 and 8, where a temporary increase in discharge capacity was seen after the cycling was restarted. These interruptions (up to days in length) did not seem to affect the overall cycle life of the cells. The transient increase in capacity may be the result of Li diffusing to locations near the surface of the cathode structure during the pause time, allowing more Li to be deintercalated. In some cases, this increase in capacity was not observed even though power interruptions had occurred.

Figure 8 illustrates cycling behavior at 0°C. At 1 mA/cm² and 75 percent DOD, the middle cycle voltage dropped to 1.75V at cycle 50 with an energy density of 34 Wh/lb. This was generally the case with all cells in this group. This particular cell achieved a maximum energy density at cycle 20 of 42 Wh/lb. The average cycle life of this test group was 102 cycles and all of the cells failed by capacity fading. When the depth of discharge was decreased to 50 percent, keeping temperature and the discharge current density the same, all three cells in this group failed on the fifth cycle by the overcharge halt condition. This surprising decrease of cycle life at the lower DOD parallels the observations at 25°C; again, its cause is not known. At 25°C, this anomaly was absent at higher current densities. (See Table 2.) A similar statement cannot be made at 0°C since no cycling was possible above 1 mA/cm². An attempt was made to cycle these cells at 5 mA/cm² and 0°C to 75 percent depth of discharge. A fresh uncycled cell would not discharge, meaning that within 1 second the voltage fell below the safety voltage cutoff of 0.8V. Another group of three cells was discharged for one cycle at 25°C and then cooled to 0°C. Cycle two was then started at 0° and this time the cells discharged for 35 minutes only to reach the 0.8V voltage trip without obtaining 75 percent depth of discharge. This discharge profile is shown in Figure 9. The mid-discharge voltage was 1.4V. These data suggest that pretreatment by cycling at 25°C, to effect the beneficial structural change, allows cells to be cycled at 5 mA/cm² and 0°C, at least up to 50 percent DOD. Figures 2 through 6 suggest that 20 to 50 prior 25°C cycles might be required to effect a substantial improvement in 0°C cycling. However, such cycling was not performed in the present study. Table 2 shows specific energies and discharge voltages of one cell collected from each test group at 25°C and 0°C.

CONCLUSIONS

Niobium Triselenide undergoes a beneficial structural change upon electrochemical lithiation. This is evident in these AA cells by their increasing voltage and capacity from cycle one to some maximum before falling off to the end of cycle life. This effect is present in the data at all test conditions in this study. The average cycle life of the cells increased as the depth of discharge decreased except at 1 mA/cm². This occurred both at 25° and 0°C.

The data in Table 2 lack the clear-cut trends expected, i.e., a deterioration in performance as temperature falls or as depth of discharge or rate of discharge rise. This is due, at least in part, to the overcharging behavior that halted cycling of 40 percent of cells tested. There appear to be two different ways whereby the overcharge criterion halts cell cycling. In the first (the dendrite shorting mechanism) both charge and discharge capacities fall until the last few cycles when charge capacity rises sharply and halts the experiment. The last charging curves exhibit noisy traces consistent with dendrite shorting which then cause the observed sharp rise in charge capacity. In the second, both charge and discharge capacities rise throughout cycling until the overcharge exceeds 20 percent and cycling is halted. The latter may derive from the beneficial structural change mentioned above. In this case the overcharge halt condition actually penalizes the cell for improving!

The test program has shed some light on the rate capability and cycle life of NbSe₃ AA cells manufactured by AT&T. At 25°C and 75 percent depth of discharge, we were able to achieve specific energies of 30 Wh/lb at cycle 1, fading to about 7 Wh/lb at cycle 100 for 10 mA/cm² discharges with no pause time. Two hundred cycles were delivered at 1 mA/cm², producing specific energies as high as 42 Wh/lb at about cycle 100, falling to 32 Wh/lb after 200 cycles, when the cells were halted. Pretreating the cells by cycling them once at 25°C enabled us to discharge the cells at 0°C greater than 1 mA/cm². At 5 mA/cm², we were able to achieve only one discharge not reaching 75 percent depth of discharge. The discharge lasted about 38 minutes, delivering 29 Wh/lb at a mid-discharge voltage of 1.40V. Cycling may be possible at lower depths of discharge or after 20 to 50 prior 25°C cycles. At 1 mA/cm² and 75 percent depth of discharge, the cells reached 42 Wh/lb near cycle 20 before fading to about 10 Wh/lb around cycle 100 also at 0°C.

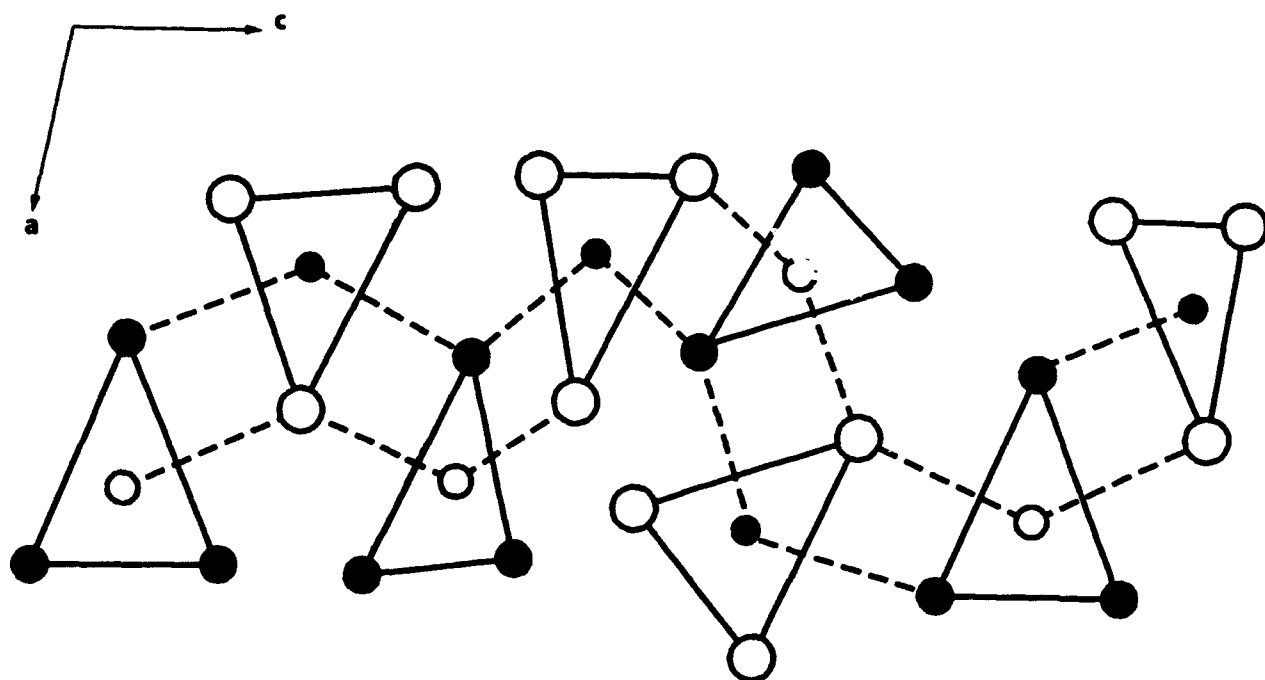


FIGURE 1. NbSe₃ UNIT CELL

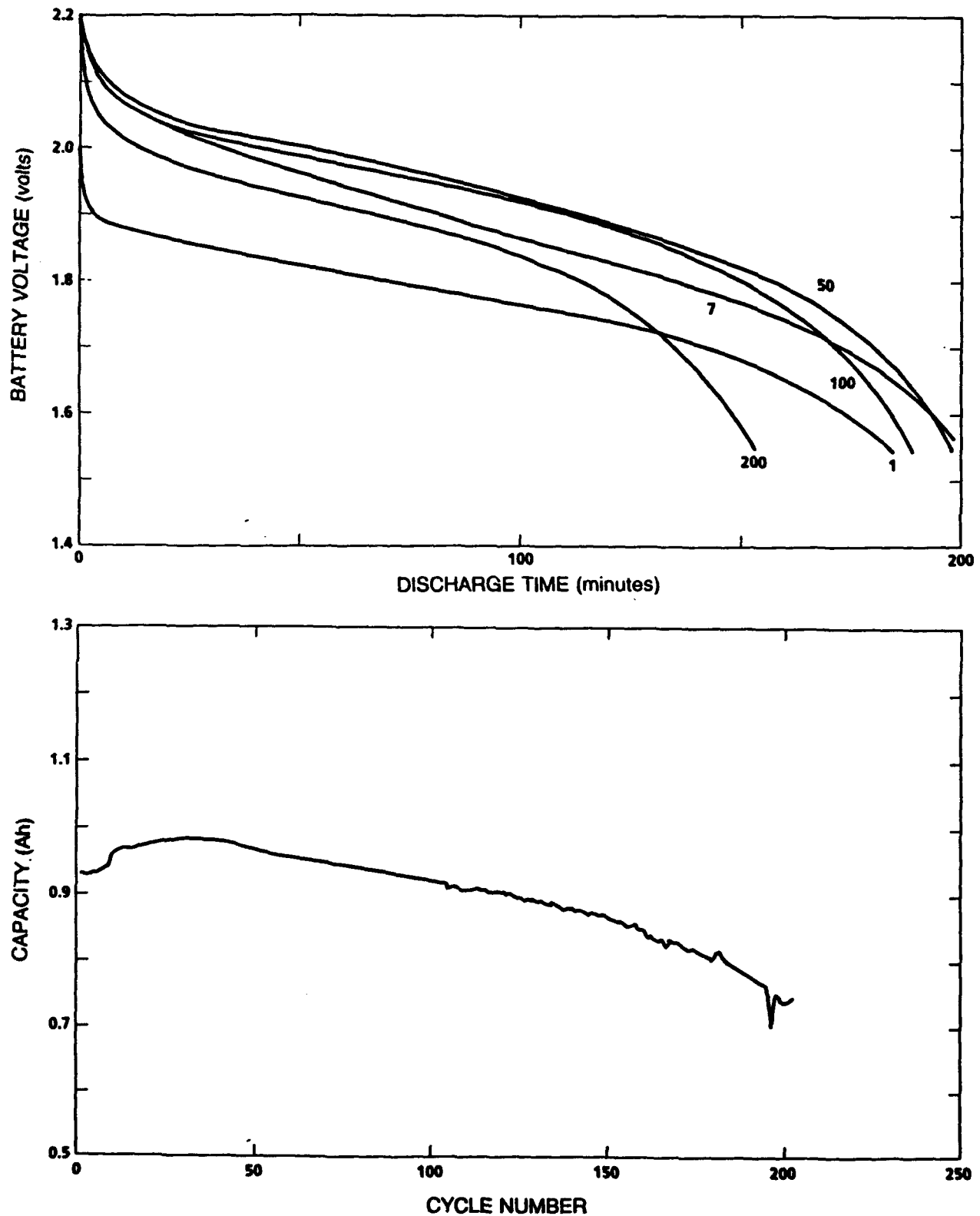


FIGURE 2. DISCHARGE CHARACTERISTICS OF Li/NbSe₃ AA CELLS AT 1mA/cm², 75% DOD, AND 25°C. CELLS WERE CYCLED BETWEEN 2.40 AND 1.55V AND CHARGED AT 0.33 mA/cm²

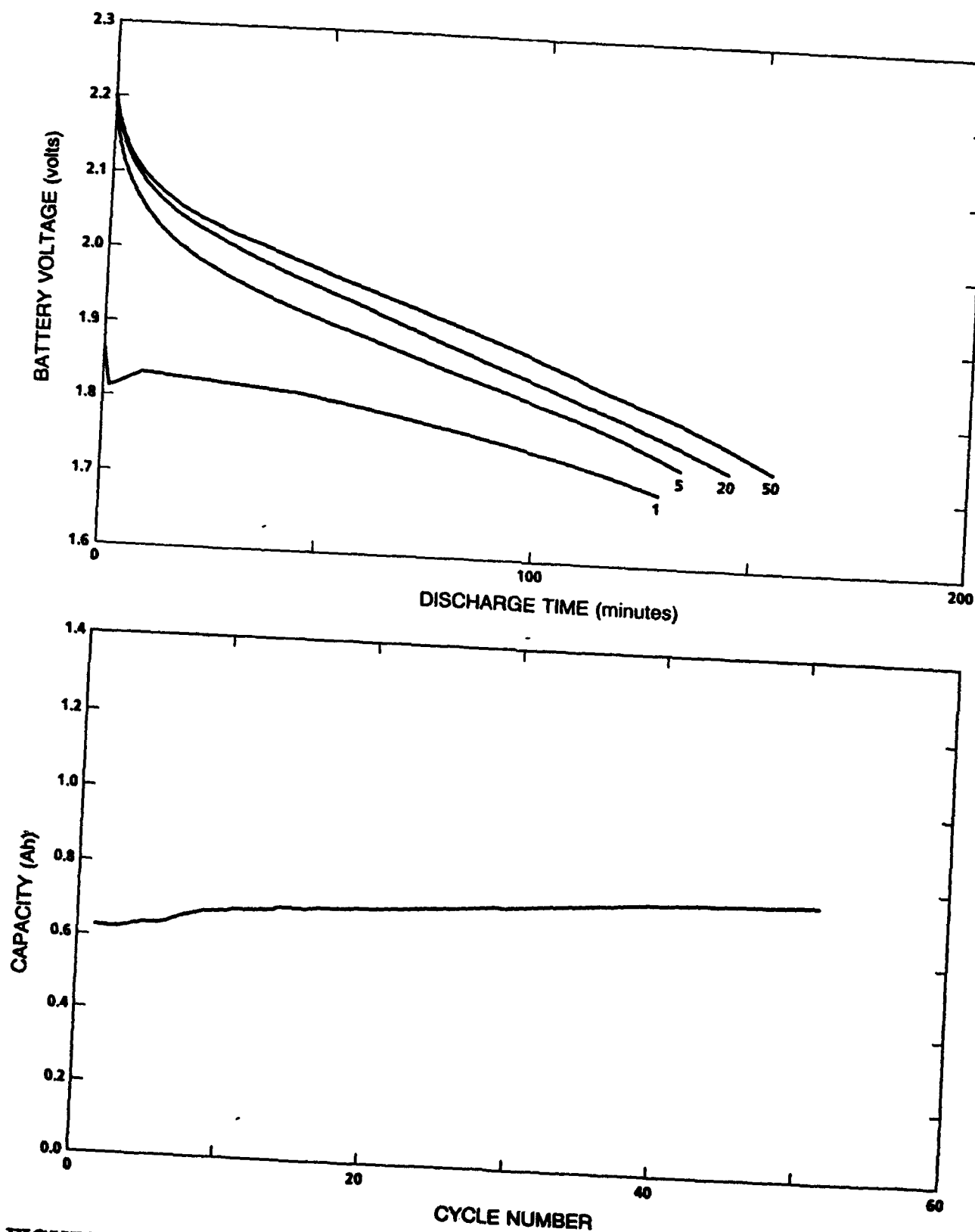


FIGURE 3. DISCHARGE CHARACTERISTICS OF Li/NbSe₃ AA CELLS AT 1mA/cm², 50% DOD, AND 25°C. CELLS WERE CYCLED BETWEEN 2.40 AND 1.74V AND CHARGED AT 0.33mA/cm².

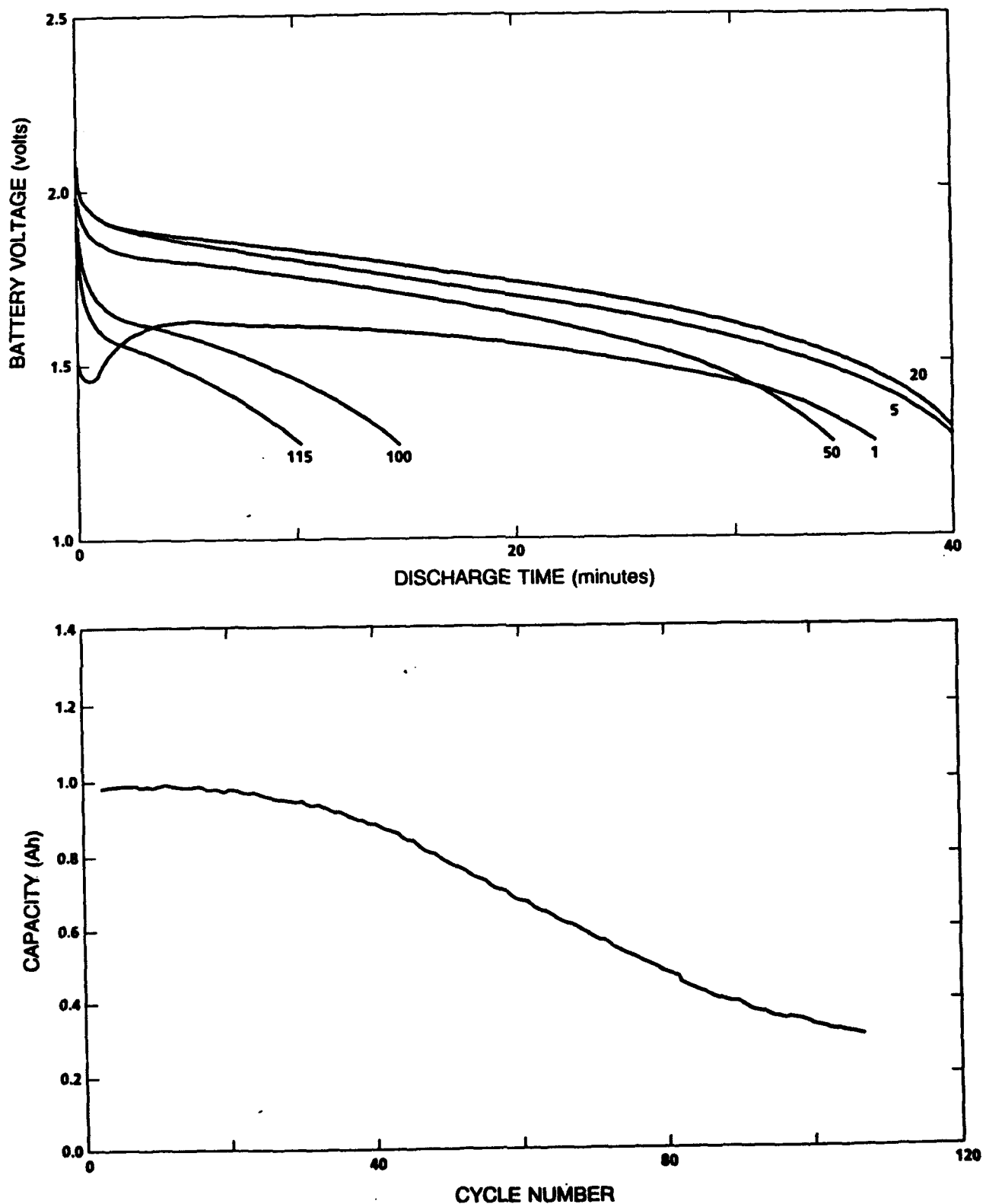


FIGURE 4. DISCHARGE CHARACTERISTICS OF Li/NbSe₃ AACELLS AT 5mA/cm², 75% DOD, AND 25°C. CELLS WERE CYCLED BETWEEN 2.40 AND 1.27V AND CHARGED AT 0.33mA/cm².

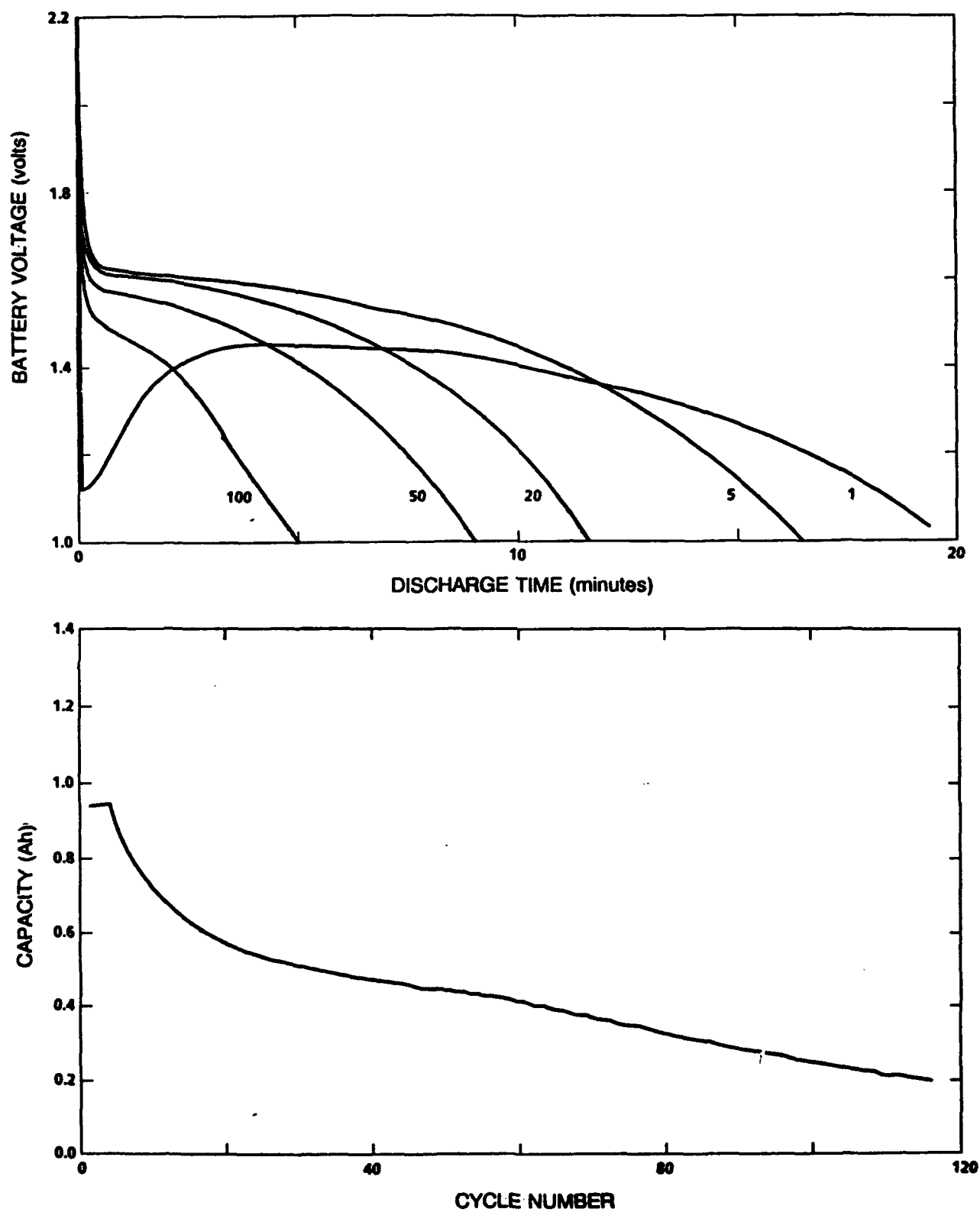


FIGURE 5. DISCHARGE CHARACTERISTICS OF Li/NbSe₃ AA CELLS AT 10mA/cm², 75% DOD, AND 25°C. CELLS WERE CYCLED BETWEEN 2.40 AND 1.00V AND CHARGED AT 0.33mA/cm²

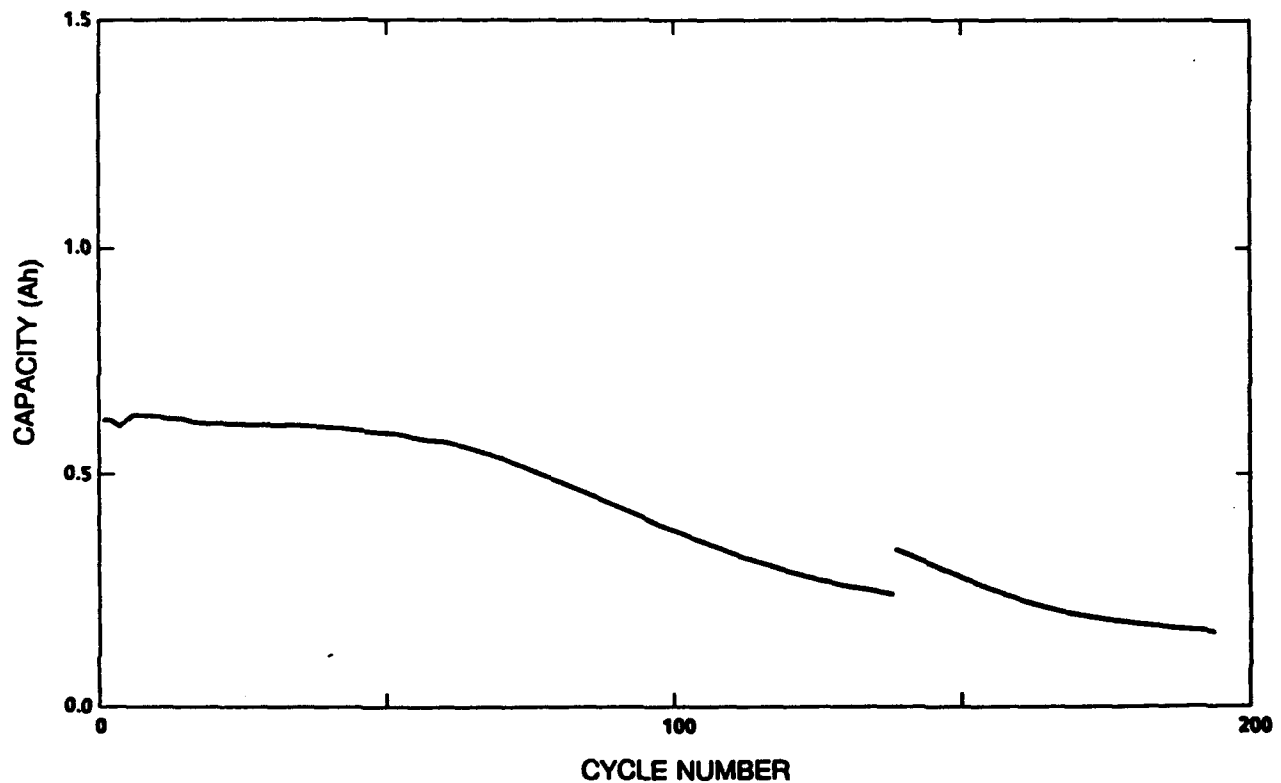
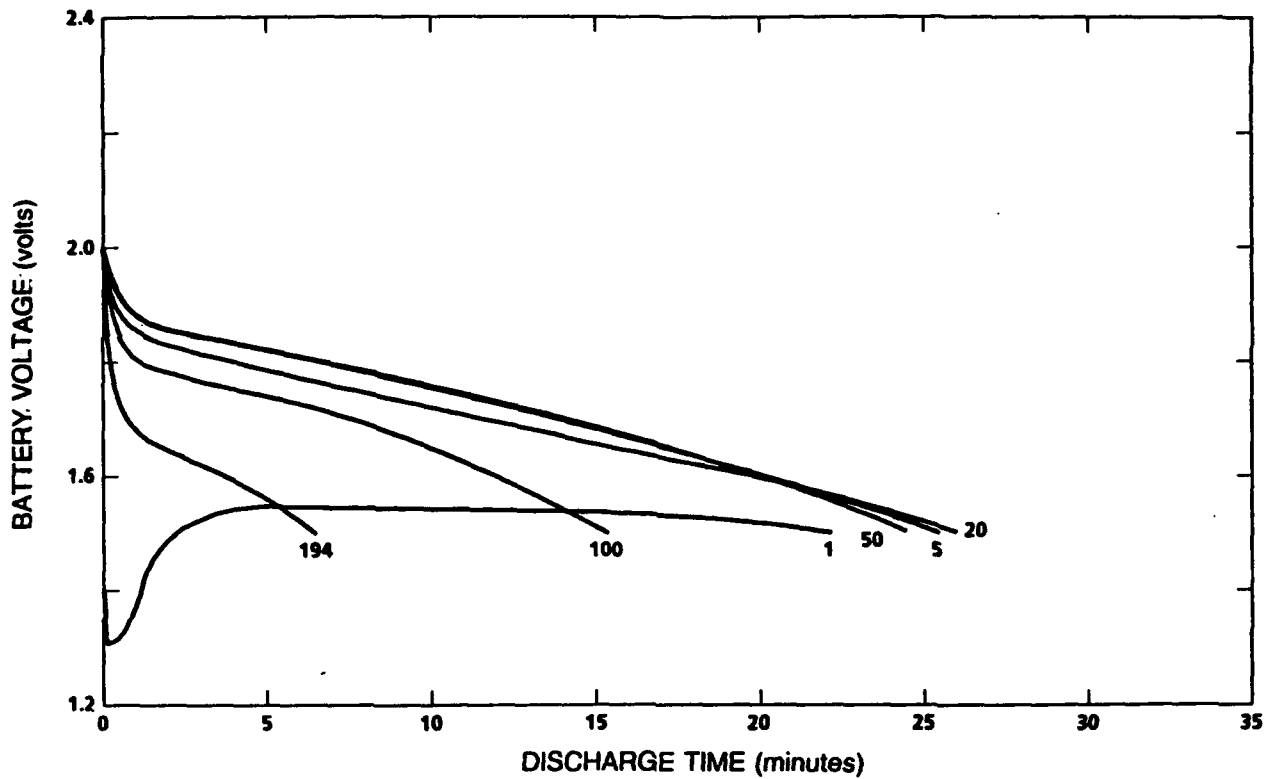


FIGURE 6. DISCHARGE CHARACTERISTICS OF Li/NbSe₃ AA CELLS AT 5mA/cm², 50% DOD, AND 25°C. CELLS WERE CYCLED BETWEEN 2.40 AND 1.51V AND CHARGED AT 0.33mA/cm²

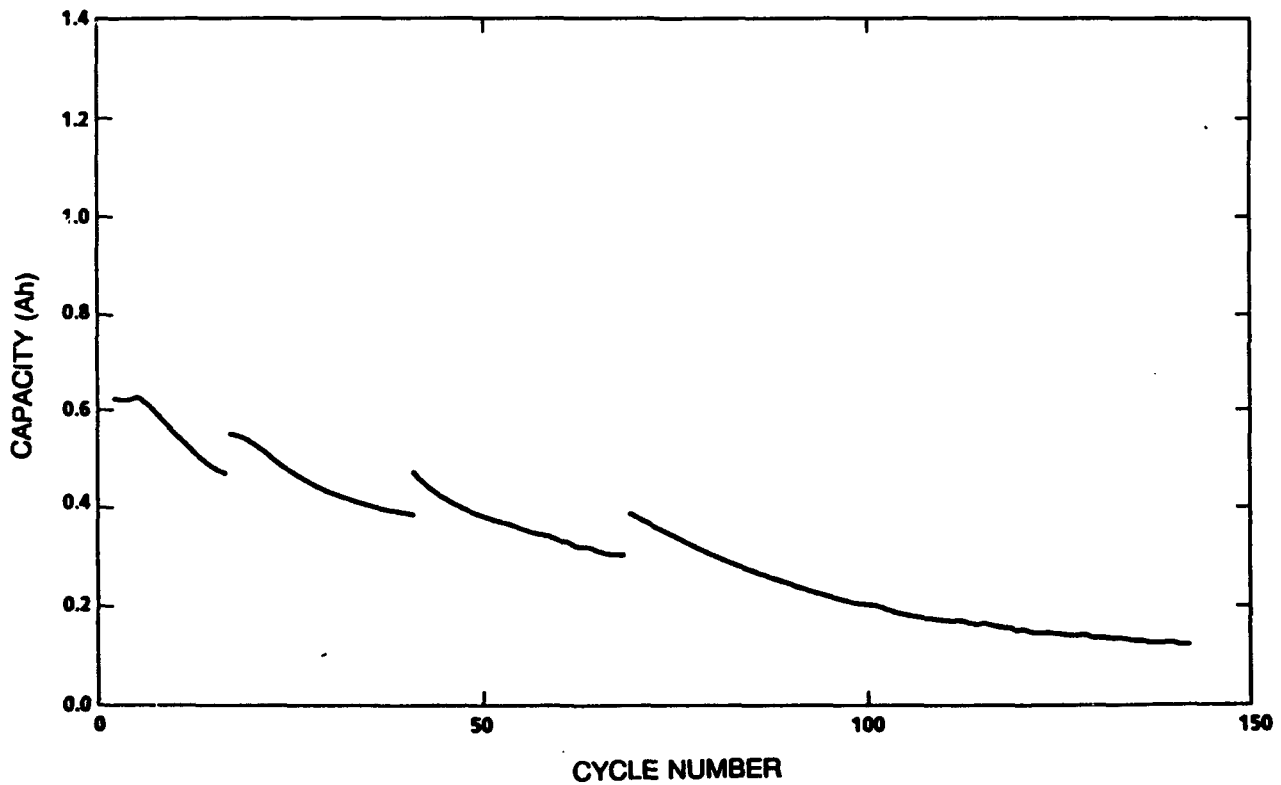
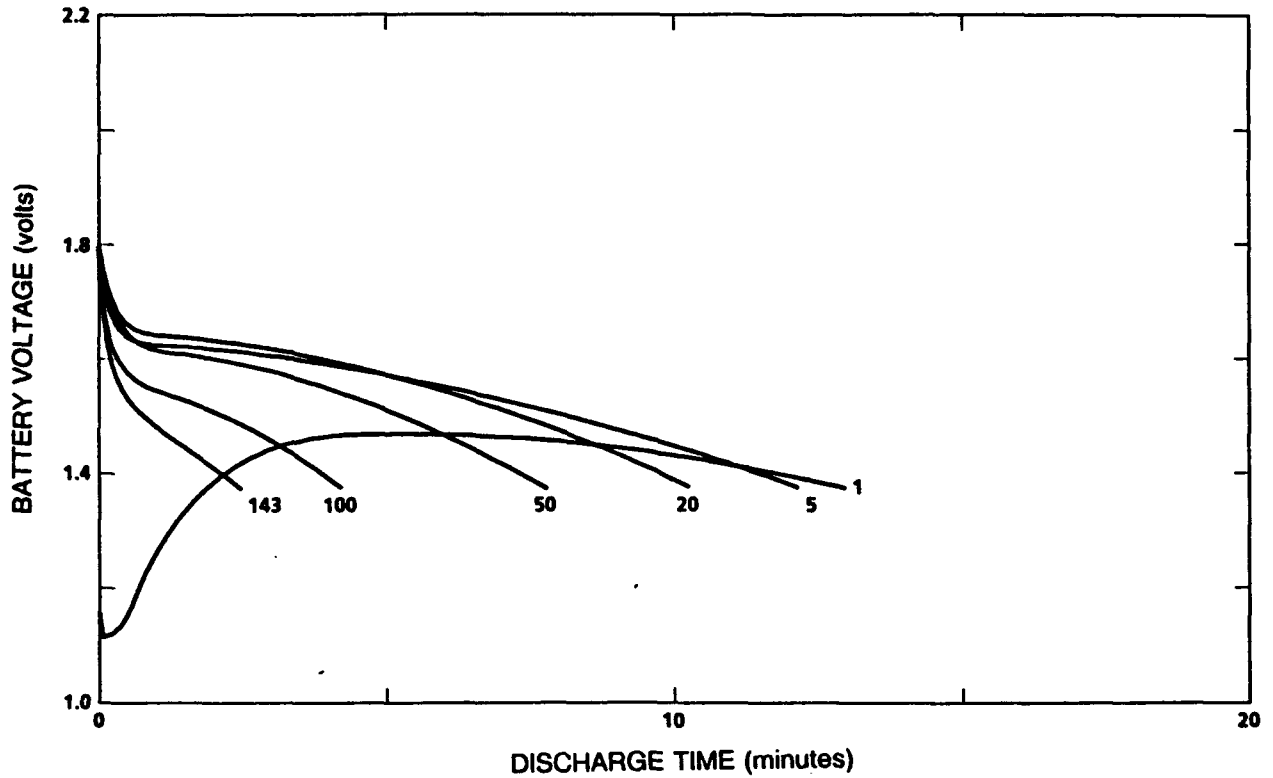


FIGURE 7. DISCHARGE CHARACTERISTICS OF Li/NbSe₃ AA CELLS AT 10mA/cm², 50% DOD, AND 25°C. CELLS WERE CYCLED BETWEEN 2.40 AND 1.37V AND CHARGED AT 0.33mA/cm²

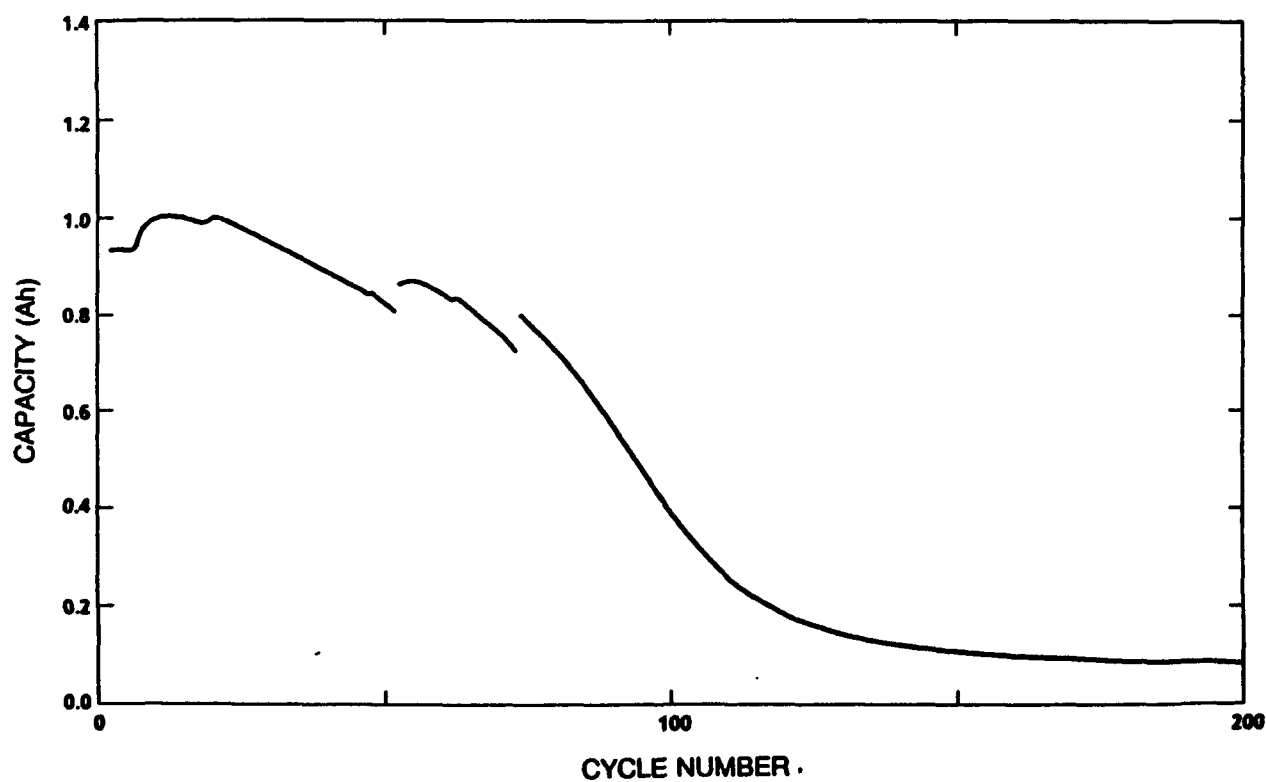
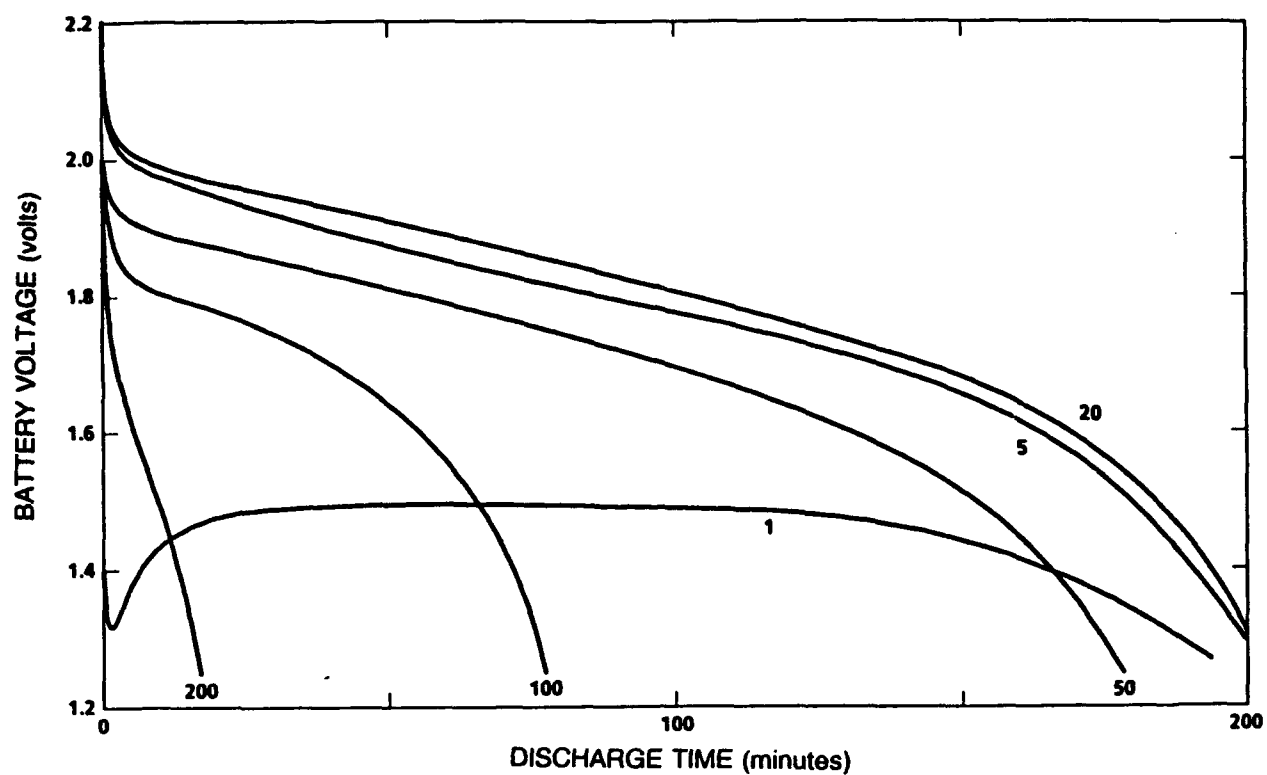


FIGURE 8. DISCHARGE CHARACTERISTICS OF Li/NbSe₃ AA CELLS AT 1mA/cm², 75% DOD, AND 0°C. CELLS WERE CYCLED BETWEEN 2.40 AND 1.25V AND CHARGED AT 0.33mA/cm²

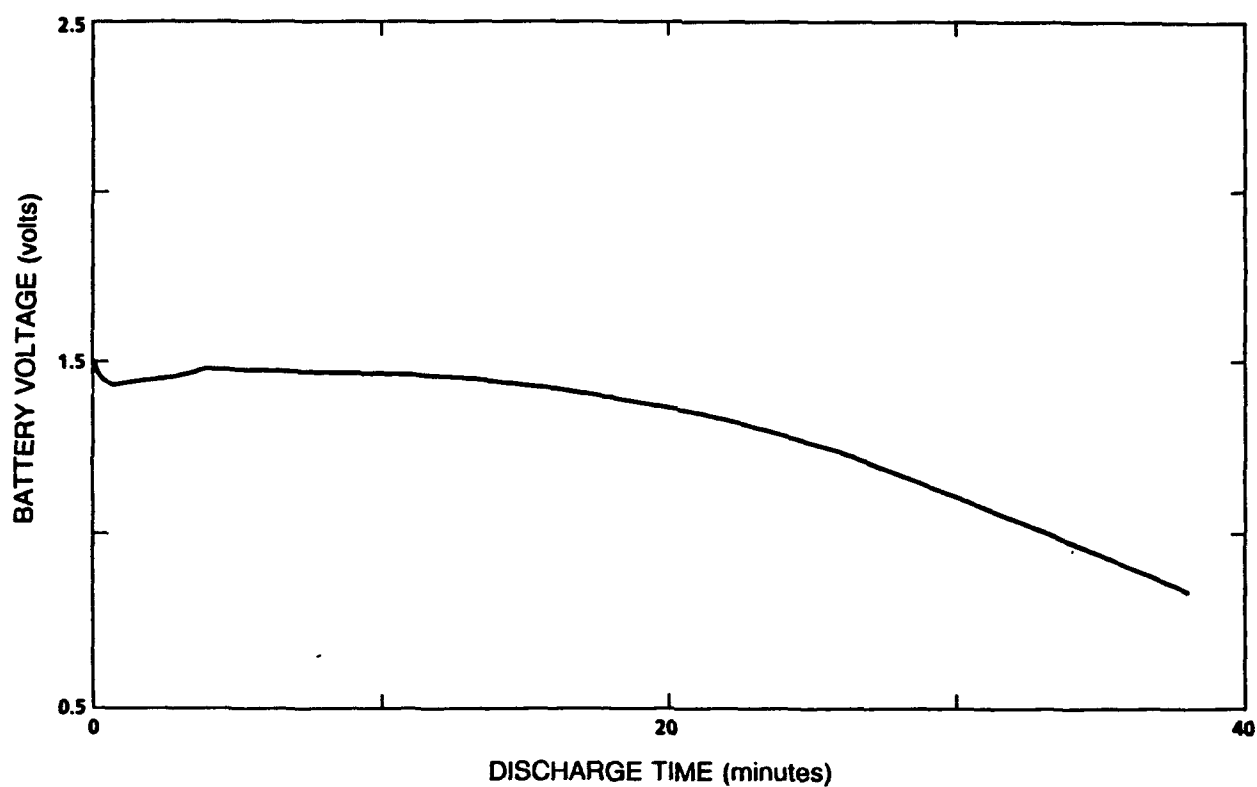


FIGURE 9. DISCHARGE CHARACTERISTICS OF Li/NbSe₃ AA CELLS AT 5mA/cm², 75% DOD, AND 0°C. DISCHARGE HALTED WHEN 0.80V MINIMUM WAS REACHED (BEFORE 75% DOD ACHIEVED)

TABLE 1. CYCLE LIFE OF Li/NbSe₃ AA CELLS AND FAILURE MODE
TEMPERATURE = 25°C

DEPTH OF DISCHARGE	CURRENT DENSITY (mA/cm ²)									
	1			5			10			END
	CELL #	CYCLES	END*	CELL #	CYCLES	END	CELL #	CYCLES	END	
75%	1708	210	HALT	1694	125	CAP	1719	111	CAP	CAP
	1699	174	HALT	1696	108	CAP	1688	89	CAP	CAP
	1720	200	HALT	1685	115	CAP	1713	100	CAP	CAP
50%	1704	22	HALT	1749	180	CAP	1771	35	HALT	HALT
	1712	50	HALT	1692	177	CAP	1746	113	CAP	CAP
	1717	32	HALT	1750	9	HALT	1691	143	CAP	CAP

*END: CAP = ACHIEVED 25% OF INITIAL CAPACITY

HALT = OVERCHARGE HALT CONDITION REACHED

TEMPERATURE = 0°C

DEPTH OF DISCHARGE	CURRENT DENSITY (mA/cm ²)									
	1			5			10			END
	CELL #	CYCLES	END*	CELL #	CYCLES	END	CELL #	CYCLES	END	
75%	1718	115	CAP	1775	1	CAP				
	1710	79	CAP	1721	1	CAP				
	1715	103	CAP	1774	1	CAP				
50%	1751	5	HALT							
	1759	5	HALT							
	1748	5	HALT							

*END: CAP = ACHIEVED 25% OF INITIAL CAPACITY

HALT = OVERCHARGE HALT CONDITION REACHED

TABLE 2. SPECIFIC ENERGIES OF Li/NbSe₃ AA CELLS
TEMPERATURE = 25°C

DEPTH OF DISCHARGE	CURRENT DENSITY (mA/cm ²)								
	1			5			10		
	<u>CYCLE #</u>	<u>V, t/2</u>	<u>Wh/lb</u>	<u>CYCLE #</u>	<u>V, t/2</u>	<u>Wh/lb</u>	<u>CYCLE #</u>	<u>V, t/2</u>	<u>Wh/lb</u>
75%	1	1.78	37	1	1.55	33	1	1.40	30
	100	1.95	42	50	1.70	34	50	1.40	14
	200	1.90	32	115	1.48	8	100	1.35	7
50%	1	1.80	23	1	1.55	19	1	1.48	21
	20	1.90	30	100	1.70	15	70	1.52	12
	50	1.92	34	177	1.60	6	143	1.45	7

TEMPERATURE = 0°C

DEPTH OF DISCHARGE	CURRENT DENSITY (mA/cm ²)								
	1			5			10		
	<u>CYCLE #</u>	<u>V, t/2</u>	<u>Wh/lb</u>	<u>CYCLE #</u>	<u>V, t/2</u>	<u>Wh/lb</u>	<u>CYCLE #</u>	<u>V, t/2</u>	<u>Wh/lb</u>
75%	1	1.50	31	1	1.40	29			
	50	1.75	34						
	115	1.70	9						
50%	1	1.61	21						
	3	1.74	29						
	5	1.80	32						

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